April 15, 1968

RESEARCH AND DEVELOPMENT OF SOLAR CELL CONTACTS

January 1 - March 31, 1968

1st Quarterly Progress Report

Prepared for

JET PROPULSION LABORATORY

CALIFORNIA INSTITUTE OF TECHNOLOGY

4800 Oak Grove Drive

Pasadena, California 91103

Contract 952145

General Precision Systems, Inc.

Librascope Group

808 Western Avenue

Glendale, California 91201

This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, sponsored by the National Aeronautics and Space Administration under Contract NAS7-100.

TABLE OF CONTENTS

INTRODUCTION

This program is directed toward JPL's objective of optimizing solar cell contacts and improving interconnections between solar cells, capable of surviving the extremes of space environments for long periods of time. This objective is largely dependent upon the achievement of an ohmic, low resistance, adherent, stable electrical contact to the solar cell. Once this is achieved, utilizing materials compatible with the interconnecting media, the task of bonding the interconnections to individual solar cells can be pursued with minimum perturbations introduced at the contact silicon interface.

The need to survive wider temperature extremes resulting from new space missions places new demands on the adherence of the electrical contact to the silicon. The primary tool used to achieve improved adherence of thin film deposited material is Librascope's proprietary Cold Substrate Deposition Process (CSDP). This process has the capability of providing a tenacious bond to the substrate and allowing careful control of purities and geometries of deposited films.

The first task of the proposed program is to conduct laboratory research and development, utilizing the CSDP, in order to achieve the desired contacts to the silicon cells. The following presentation is centered first on a discussion of CSDP followed by a discussion of the criteria for material selection, and of the test results obtained during the first quarterly reporting period.

COLD SUBSTRATE DEPOSITION PROCESS

Conventional deposition processes require heated cycles of temperatures to obtain a strong mechanical bond. For solar cells, the heating cycle necessitates very careful control to achieve the requisite alloying and/or diffusion reaction while confining it within the one micron depth of the upper surface. Excessive temperature or extended exposure to high temperatures may lead to short circuiting of the junction, while low temperatures and short elevated temperature cycles may lead to weak bonds.

Librascope's Cold Substrate Deposition Process (CSDP) was developed specifically to achieve maximum adherence of thin films and, at the same time, to provide maximum density of the material deposited. The adhesion of the deposited films is superior to that obtained by standard depositions because the activation energies responsible for the adhesion are controlled and localized on a microscopic scale within the substrate-deposit interface. The improvement of the adherence of the bond is achieved because of the uniformity of the bonding forces over the entire contacting surface and the elimination of those stresses which occur when excessive localized heterogeneous alloying occurs.

As developed, the CSDP permits the deposition of a wide range of materials onto a wide range of substrates. The process provides a ready means for adjusting and controlling the parameters of the deposition. By achieving unique control of the deposition parameters, certain properties of the impinging particles can be varied over wide ranges. As a consequence, the characteristics of the thin films can be modified and controlled to a remarkable degree. The process provides means for independently controlled cleaning of the substrate both before and during the deposition. Further, the CSDP excels in the ability to achieve adherent deposits of material on substrates without heating the bulk of the substrate and without resorting to post-deposition annealing treatments. Since the depositions are performed on unheated substrates, the temperature sensitive properties, both crystallographic and functional, remain unaffected. In other words, all harmful effects of elevated temperatures normally required are eliminated since the rest of the material, with the exception of a very thin surface zone, is maintained at relatively low temperatures. In particular, silicon solar cell efficiency is not degraded.

Higher conductivity occurs in CSDP films because the process leads to purer and denser deposits. Purity is enhanced by concurrent removal of a controlled portion of material on the substrate, thereby removing undesired contaminants. High density is obtained by providing sufficient mobility in the depositant to provide excellent continuity in the deposit without the usual island structure characteristic of heterogeneous nucleation in standard vacuum deposition processes. These features can be achieved with CSDP while still maintaining a high rate of deposition.

Summarizing, the important advantages of the CSDP which have been verified are as follows:

a) It permits direct deposition on temperature-sensitive substrates, devices and circuits;

b) It permits the ready use of photoresists in the fabrication of high density circuits;

c) It permits the use of moderately high vacua because of the self cleaning action of the process, with attendant cost saving and operational simplicity;

d) It provides independently controllable means for argon (or other inert gas) cleaning of the substrate before, during, or after the deposition;

e) It provides control over the substrate-depositant interface characteristics and the depositant properties.

MATERIALS SELECTION

Historically, the gradual increase in efficiency of silicon solar cells can be traced largely to the improvement in the grid design and to the shift in grid material from electroless nickel to a titanium-silver contact material. The latter has a distinctly lower resistance than the nickel formerly used and provides improved adherence.

Achievement of the optimum electrical contact between the grid electrode and silicon is inherently a very difficult problem. The difficulty stems from the fact that the optimum p-n junction depth is within one micron of the upper surface (so as to achieve maximum photon absorption). The desired properties of the grid electrical contact are ohmicity, low resistance, adherence, stability, high mechanical strength, and the ability to be electrically connected to an interconnecting wire or ribbon. Despite the difficulties, adherent titanium-silver grid contacts have been made successfully in production quantities for several years. Titanium-silver was chosen as the grid contact material primarily because of its low resistivity and its solderability. The principal problems with the titanium-silver contact are the loss of adherence at low temperatures because of the mismatch in temperature coefficient of expansion compared to silicon, weakening of the bond on exposure to moisture because of a chemical reaction with silver, and long-term loss of adherence, presumably because of the conversion of titanium to titanium dioxide.

Operationally, new NASA space missions require exposing the panels to wider temperature and environmental extremes, and, as a result, some of the limitations of the titanium-silver contact have become apparent. The availability of new techniques and equipment (such as Librascope's CSDP) which provide the requisite adherence in the interfacial region, the desired conductivity in a grid electrode 1.5 to 2 microns thick, and compatibility with solderless inter-connection theory and practice permits the use of other materials which are superior to titanium-silver.

Several candidate materials were considered for electrical contact to silicon (see Table I).

TABLE I

POTENTIAL LOW RESISTIVITY GRID MATERIALS

Material	Room Temperature Coeff. of Expansion $\Delta \ell / \ell$ C x 10^{-6}	Resistivity μ - ohm cm	Remarks
Cu	16.8	1.67	Contaminates Si
Ag	18.8	1.59	(Adherence problem Humidity reaction)
Au	14.3	2.19	Adherence problem
Aℓ	25.5	2.65	High reflection
Mo	4.9	5.17	High resistivity
Ni	12.8	6.84	High resistivity
Cr	6.8	13.0	High resistivity

The major material properties considered were resistivity and coefficient of expansion of the respective materials. A review of these and other properties indicates that aluminum has the best combination of properties for the following reasons:

a) Aluminum exhibits good adherence to silicon. Silicon having a high affinity for oxygen (free energy of oxide formation = 194.7 Kcal/mole) is always coated with an oxide layer which prevents the reaction of silicon with most metals. Aluminum has an even stronger affinity for oxygen than has silicon (free energy of aluminum oxide formation = 376.7 Kcal/mole) and can therefore penetrate the oxide layer and form a bond with silicon.

b) Aluminum has a high volume conductivity and is the fourth best electrical conductor.

c) Aluminum provides an ohmic and low resistance contact to silicon.

d) Aluminum is a light-weight metal, suitable for solar cell assemblies.

e) Aluminum has high corrosion resistance.

f) The presence of aluminum in a silicon crystal does not adversely affect the performance of the p-n junction.

g) Since an aluminum tab can be bonded to aluminum, a one-metal bonding material system can be achieved. This will eliminate long-term galvanic reactions which occur when dissimilar metals are used for bonding.

The relatively high temperature coefficient of expansion of aluminum is a matter of some concern and indicates that a trade-off will be required between adequate thickness to maintain low resistance and minimum thickness to prevent excessive stress in the conductor. The temperature coefficient of expansion of aluminum in the range -191° to $+16^{\circ}C$ is 18.35×10^{-6} while that of silver in the same range is 17.04×10^{-6}. On this criterion, therefore, aluminum is slightly inferior to the currently used contact material.

Due to its low resistivity and relatively low temperature coefficient of expansion, gold is an intriguing candidate as an effective grid contact material. Although gold normally has only marginal adherence, it is anticipated that the adherence will be enhanced through the use of Librascope's CSDP. A material system with gold grid electrodes and gold plated molybdenum wire interconnections may have wider temperature range than a material system with aluminum thin film grid electrodes and aluminum interconnecting wires.

Both gold and aluminum are excellent reflectors of near infrared radiation so that both materials can be used for the back contact to increase efficiency. The advantages of a reflecting back are*:
(1) increased infrared rejection to minimize heating of the cell and
(2) increased useful absorption of radiation in the range just beyond one micron.

Neither aluminum nor gold electrodes have been utilized to date, primarily because no technique has been available to achieve sufficient adherence to silicon without degrading the junction which lies a mere one micron beneath the surface. It appears, therefore, that a technique such as CSDP which will achieve adherence of gold to silicon, or the techniques which will achieve maximum conductivity per cross-sectional area of aluminum will lead to improved grid contacts which are capable of survival at low temperatures and will be stable for long periods of time.

EXPERIMENTAL RESULTS

The first major task undertaken was to achieve adherent aluminum films to n-type silicon. This task was undertaken first as it is the most difficult task in that the technique used must not generate local p-n junctions (substitutional aluminum renders silicon p-type if there are insufficient n-type impurities in the n-type silicon). Fortunately, the doping level is so high in solar cells that the accomplishment of adherence without forming the undesired localized junctions was attained by systematically varying the critical parameters of the CDSP in the vacuum chamber until the optimum contact-silicon interface was achieved. The thickness of the aluminum films deposited on the heavily doped n-type silicon ranged between 1.5 - 2.0 microns. The effect of glow discharge cleaning on the properties of a silicon wafer was investigated experimentally and evaluated in terms of the current-voltage characteristics of the aluminum contacts deposited on the ion-cleaned surface. Chemically polished wafers were cleaned by ion bombardment from a glow discharge prior to deposition. The glow discharge was established in 20 microns Hg pressure of argon gas, and the applied potential was 4000 volts A.C. The time of exposure to the ion impact was 10 minutes. Aluminum was then deposited through a metal mask by standard evaporation techniques onto an unheated substrate. The thickness of the deposited aluminum film was 1.5 microns, and the contacts were in bands 2.5 mm wide with 1.5 mm separation. The current-voltage characteristic of the contact was observed with a transistor curve tracer (see Figure 1). The current showed a nonlinear voltage relationship, with the contact resistance being approximately 25 ohms.

The glow discharge cleaning experiment was repeated under similar conditions as applied during the previous experiment with the exception that the exposure to the ion impact of the glow discharge cleaning was increased to 30 minutes. The current-voltage characteristics of this contact (see Figure 2) again showed a nonlinear relationship, more pronounced than in the previous case. The resistance varied exponentially with the applied voltage, being initially approximately 125 ohms up to 0.15 volts, and decreasing to about 10 ohms above 0.15 volts. The photosensitivity of the contacts deposited during these two experiments was tested qualitatively with a 250-watt, unfiltered tungsten light source (see Figures 3 and 4). The contact deposited on silicon which had been subjected to a 30-minute glow discharge cleaning. The conclusion to be drawn from these experiments is that a glow discharge treatment, which is usually employed as a cleaning procedure of substrates prior to the deposition, is not applicable to active substrates, such as silicon, for deposition of metals when ohmicity of the contact is required.

As another experiment, the glow discharge cleaning was omitted and aluminum was deposited directly onto a chemically cleaned silicon wafer. The resulting current-voltage characteristic was similar to that obtained in the first experiment (see Figure 5). The contact resistance was approximately 40 ohms. The silicon wafer with the deposited aluminum contacts was then subjected to a post-deposition heat treatment in an argon atmosphere for 15 minutes at 450°C, and the current-voltage characteristic was observed (see Figure 6). As a result of the heat treatment, the characteristic became linear; and the resistance of the contact decreased to 20 ohms. Reproducibility of the results was established by the duplication of results obtained from previous experiments. Next, aluminum was deposited on an unheated, chemically cleaned silicon wafer, without a preliminary glow discharge cleaning via Librascope's proprietary CSDP. The aluminum vapor was partially ionized, and the resulting aluminum ions were transported to the substrate (silicon wafer) where they were deposited with a maximum energy of 200 ev. This corresponds to an average ion energy of approximately 112 ev, which is commensurate with sputtering energies. This energy is of sufficient magnitude to remove the oxide layer from the surface, yet is not large enough to cause formation of a junction. The characteristic revealed a current which showed a strictly ohmic relationship with the applied voltage (see Figure 7), and the contact resistance was 7 ohms.

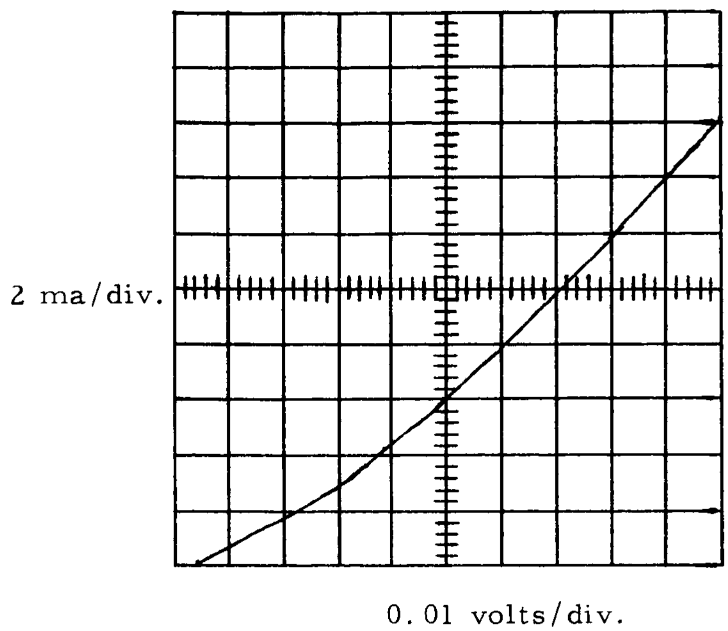
In order to establish whether this energy value (200 ev maximum) represents an optimum deposition condition, an experiment where the ions had a maximum energy of 100 ev, and another experiment with a maximum energy of 300 ev were performed. The results of these experiments showed that the current-voltage characteristic of the contact form with 100 ev ions is nonohmic at lower voltages and changes to a linear relationship at higher voltages. This voltage dependency is similar to that found for a point contact diode. The contact formed with 300-ev ions showed the presence of a p-n junction and exhibited the characteristic photoresponse.

Summarizing, the optimum condition for the formation of an ohmic, aluminum contact to n-type silicon with Librascope's Cold Substrate Deposition Process was established with aluminum ions having a maximum energy on the order of 200 ev.

After achieving adherent films to n-type silicon wafers, the technique perfected with these n-type wafers was applied to the deposition of aluminum films on p-type wafers. The aluminum was deposited on an unheated, chemically clean p-type silicon wafer without preliminary glow discharge cleaning. The aluminum vapor was partially ionized, and the resulting ions deposited with a maximum impacting energy of 200 ev. The characteristic of the contact displayed a linear current-voltage relationship (see Figure 8), and the contact resistance was 200 ohms.

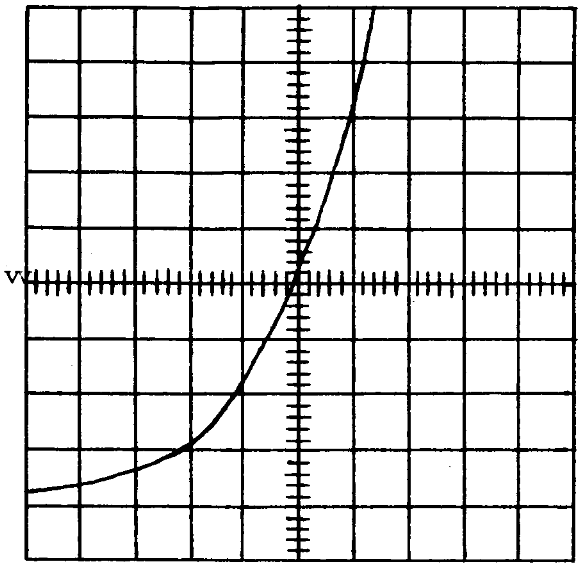
PROJECTED WORK

The technical milestones as specified for this program are shown in Figure 9. The triangles in Figure 9 represent the anticipated completion date for each of the listed milestones. The circles surrounding some of the triangles indicate which of the milestones have already been successfully met. As shown in Figure 9, and as discussed in the preceding report, Task A, which involves the aluminum contacts to n-type silicon, and Task B, which involves the aluminum contacts to p-type silicon, have already been completed. Task C, which involves making aluminum contacts to fabricated solar cells, is now in progress. For this Task, aluminum will be deposited on diffused junction silicon solar cell slices. This will involve the deposition of a conventional grid electrode and back electrode to the diffused junction silicon material purchased from a solar cell manufacturer. The current-voltage characteristic curves of the completed solar cells will be measured using pressure contacts.



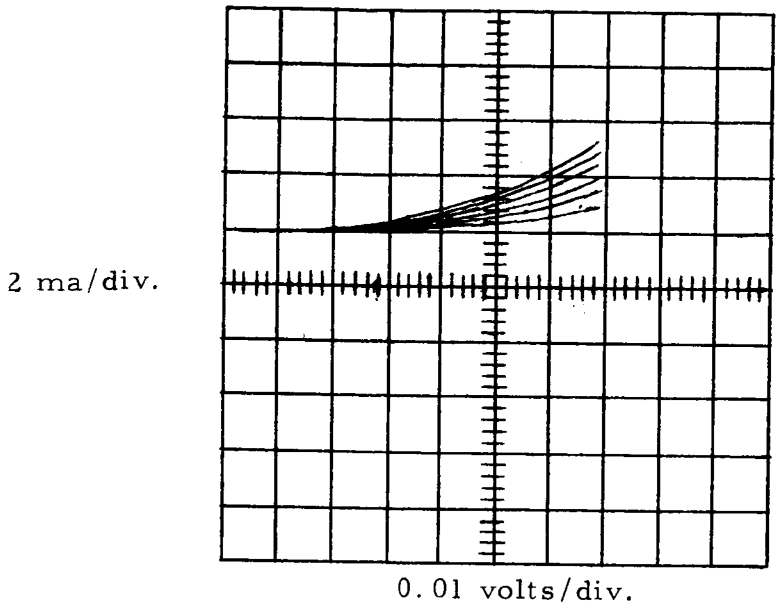
Wafer	N-type silicon (0.0009 Ω -cm)
Electrodes	Aluminum, 1.5 microns
Glow discharge cleaning	Argon, 10 minutes
Deposition process	Standard vacuum deposition
Ambient test temperature	23°C.

Figure 1. Tracing of oscilloscope display of I-V characteristics



Wafer	N-type silicon (0. 0009 Ω-cm)
Electrodes	Aluminum, 1. 5 microns
Glow discharge cleaning	Argon, 30 minutes
Deposition process	Standard vacuum deposition
Ambient test temperature	23°C.

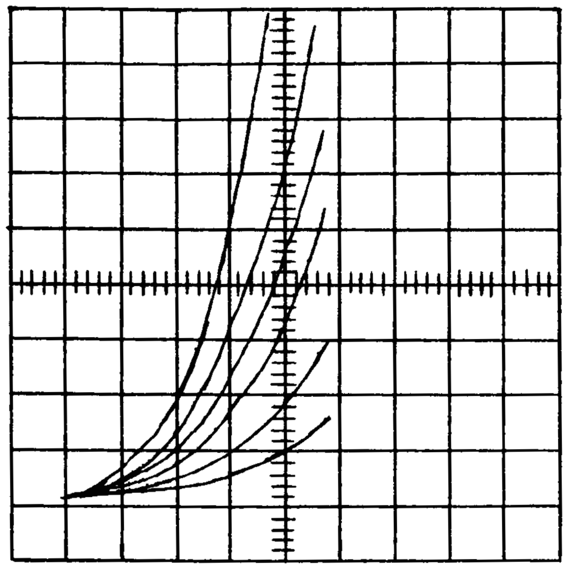
Figure 2. Tracing of oscilloscope display of I-V characteristics



Wafer	N-type silicon
Electrodes	Aluminum, 1.5 microns
Glow discharge cleaning	Argon, 10 minutes
Deposition process	CSDP, 200 volts
Ambient test temperature	23°C.

Figure 3. Tracing of oscilloscope display of photoresponse (corresponds to Figure 1.)

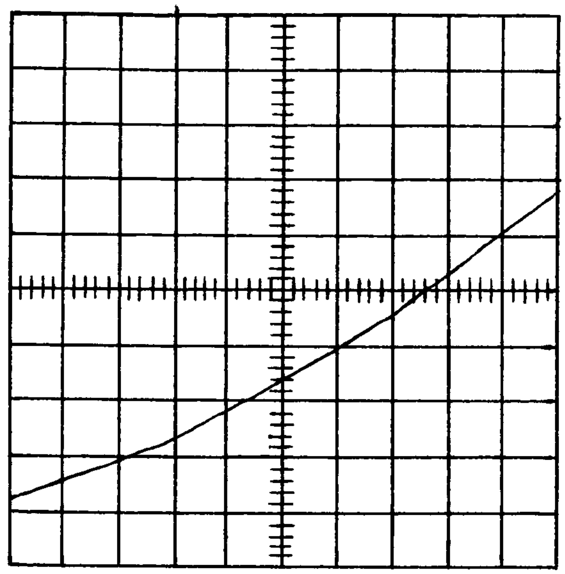
2 ma/div.



0.01 volts/div.

Wafer	N-type silicon
Electrodes	Aluminum, 1.5 microns
Glow discharge cleaning	Argon, 30 minutes
Deposition process	CDSP, 200 volts
Ambient test temperature	$23^{o}C$

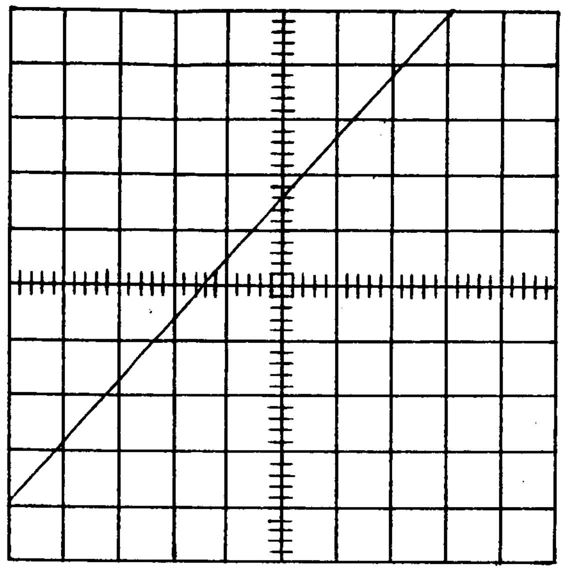
Figure 4. Tracing of oscilloscope display of photoresponse (corresponds to Figure 2.)



Wafer	N-type silicon (0.0009 Ω-cm)
Electrodes	Aluminum, 1.5 microns
Glow discharge cleaning	None
Deposition process	Standard vacuum deposition
Ambient test temperature	23°C.
Post-deposition heat treatment	None

Figure 5. Tracing of oscilloscope display of I-V characteristics

2 ma/div.

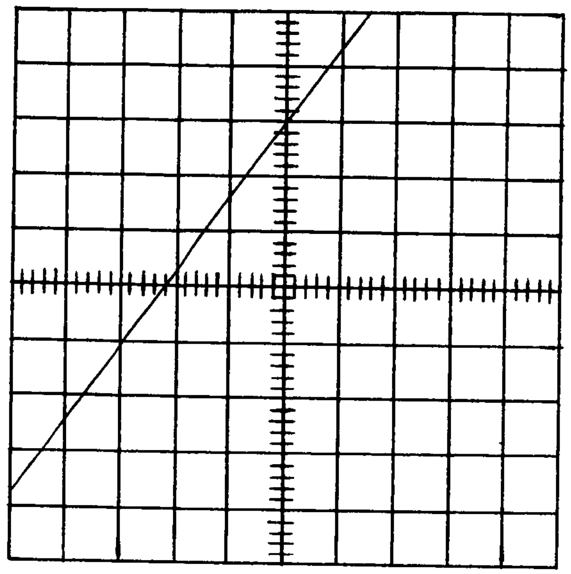


0.05 volts/div.

Wafer	N-type silicon (0.0009 Ω-cm)
Electrodes	Aluminum, 1.5 microns
Glow discharge cleaning	None
Deposition process	Vacuum deposition
Ambient test temperature	23°C.
Post-deposition heat treatment	450°C. for 15 minutes (argon atmosphere)

Figure 6. Tracing of oscilloscope display of I-V characteristics

2 ma/div.

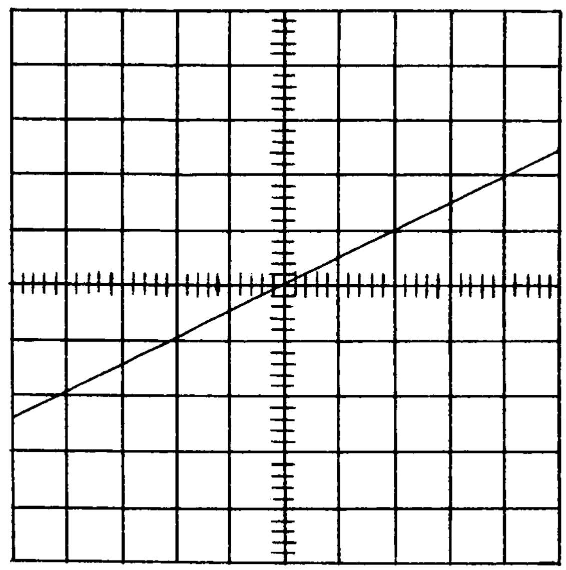


0.05 volts/div.

Wafer	N-type silicon (0.0009 Ω-cm)
Electrodes	Aluminum, 1.5 microns
Glow discharge cleaning	None
Deposition process	CDSP, 200 volts
Ambient test temperature	$23^{o}C$.

Figure 7. Tracing of oscilloscope display of I-V characteristics

0.1 ma/div.



0.01 volts/div.

Wafer	P-type silicon
Electrodes	Aluminum, 1.5 microns
Glow discharge cleaning	None
Deposition process	CDSP, 200 volts
Ambient test temperature	23°C.

Figure 8. Tracing of oscilloscope display of I-V characteristics

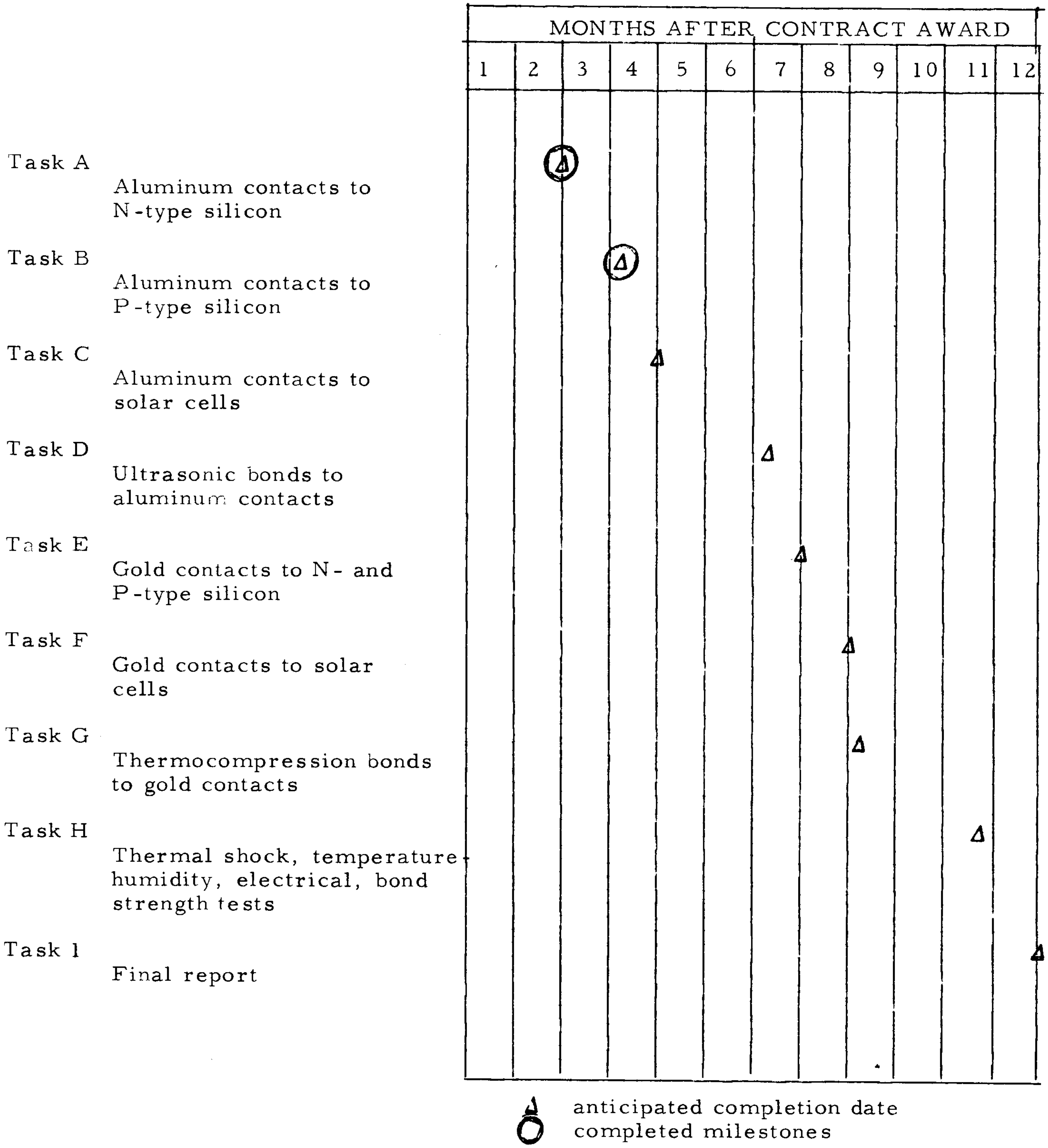


Figure 9. Technical milestones

BIBLIOGRAPHY

Baum, G. A. "Low-Energy Accelerated Ion Deposition" Report on AEC Contract AT(29-1)-1106, 6 Feb. 1967.

Kingsbury, Edwin F. and Ohl, Russell S. "Photoelectric Properties of Ionically Bombarded Silicon" Bell Sys. Tech. J. 31, 802-815 (1952)

Lewis, B. and Campbell, D. S. "Nucleation and Initial-Growth Behavior of Thin-Film Deposits" J. Vac. Sc. and Technol. 4, 209-218 (1967).

Strack, Hans "Ion Bombardment of Silicon in a Glow Discharge" J. Appl. Phys. 34, 2405-2409 (1963)